

POTENTIAL CONSTANTS AND CALCULATED THERMODYNAMIC PROPERTIES OF NITRYL FLUORIDE AND NITRYL CHLORIDE

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ABSTRACT. Using a most general quadratic potential energy expression the molecule NO_2R , where R is either F or Cl, is subjected to normal coordinate treatment. Two sets of thirteen force constants for each molecule have been proposed, and the fundamental frequencies have been calculated with the help of Wilson's F-G matrix method. The calculated and the observed values of the frequencies closely agree. Thermodynamic properties for the fluoride and the chloride have been calculated for temperatures in the range of 100-1000 °K.

I. INTRODUCTION

The infrared and Raman spectra of nitryl fluoride are reported by Rolfe and Woodward (1956) and that of nitryl chloride have been studied by Ryason and Wilson (1954). The latter authors have assigned the frequencies of the chloride molecule. Assuming the valence force potential function Hariharan (1958) has used the observed values of the frequencies and calculated the force constants by using Wilson's F-G matrix method and assigned the fundamental frequencies of both the molecules. His assignments differ from those of Ryason and Wilson so far as frequencies 651 and 411 cm^{-1} are concerned. Ryason and Wilson have assigned 651 cm^{-1} to class A_1 and 411 cm^{-1} to class B_2 , whereas Hariharan has reversed the assignments. Hariharan has neglected most of the interaction force constants and his value for f_a in the case of nitryl fluoride is negative which cannot be justified.

With a view to checking the earlier assignments the authors, using a most general quadratic potential energy expression, and assuming a planar configuration for the molecules and the point group C_{2v} , have carried out normal coordinate treatment, according to Wilson's F-G matrix method.

II. NORMAL COORDINATE TREATMENT

The planar configuration of NO_2R where R can be either F or Cl has a symmetry of C_{2v} point group ($3A_1$, $2B_2$, B_2). The symbols used for the equilibrium values of bond distances and interbond angles are shown in Fig. 1.

The examples of possible types of potential constants arising out of various types of interactions are given below.

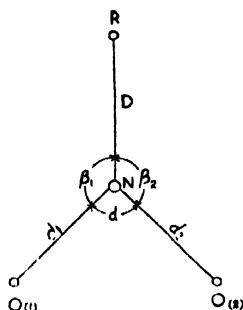


Fig. 1.

f_d = N-O stretching constant.

f_α = <O-N-O bending constant.

$f_{\beta\beta}$ = <R-N-O(1) and <R-N-O(2) angle angle interaction constant.

f_d^d = N-O(1) and N-O(2) bond bond interaction constant.

$f'_d{}^\beta$ = N-O(1) and <R-N-O(2) bond angle interaction constant.

The most general quadratic expression for potential energy is

$$2V = f_D(\Delta D)^2 + f_d\{(\Delta d_1)^2 + (\Delta d_2)^2\} + d^2 f_\alpha (\Delta \alpha)^2 + d^2 f_\beta \{(\Delta \beta_1)^2 + (\Delta \beta_2)^2\} + 2f_d^d \Delta d_1 \Delta d_2 + \\ + 2f_D^d \Delta D (\Delta d_1 + \Delta d_2) + 2df_D^\alpha \Delta D \Delta \alpha + 2df_d^\beta \Delta d (\Delta \beta_1 + \Delta \beta_2) + 2df_d^\alpha (\Delta d_1 + \Delta d_2) \Delta \alpha \\ + 2d^2 f_\alpha^\beta \Delta \alpha (\Delta \beta_1 + \Delta \beta_2) + 2d^2 f_\beta^\beta \Delta \beta_1 \Delta \beta_2 + 2df_D^\beta \Delta D (\Delta \beta_1 + \Delta \beta_2).$$

The symmetry coordinates for A_1 type of vibrations are :

$$R_1 = \Delta D.$$

$$R_2 = 1/\sqrt{2}(\Delta d_1 + \Delta d_2).$$

$$R_3 = 1/\sqrt{6}(2\Delta \alpha - \Delta \beta_1 - \Delta \beta_2).$$

$$R_4 = 1/\sqrt{3}(\Delta \alpha + \Delta \beta_1 + \Delta \beta_2) = 0 \quad (\text{Redundant}).$$

For B_1 type :-

$$R_5 = 1/\sqrt{2}(\Delta d_1 - \Delta d_2).$$

$$R_6 = 1/\sqrt{2}(\Delta \beta_1 - \Delta \beta_2).$$

For type B_2 (Out of plane)

$$R_7 = d\Delta \gamma.$$

The symmetry coordinates are normalized and orthogonal. From the potential energy matrix i.e. 'f' matrix and the matrix formed by the coefficients

contained in the symmetry coordinated the following 'F' matrix elements are obtained.

The 'F' matrix elements are

For type A_1

$$F_{11} = f_D$$

$$F_{12} = \sqrt{2}f_D^d.$$

$$F_{13} = \sqrt{(2/3)}d(f_D^a - f_D^b).$$

$$F_{22} = f_d + f_d^d.$$

$$F_{23} = 1/\sqrt{3}d(2f_d^a - f_d^b - f_d'^b).$$

$$F_{33} = 1/3d^2(2f_a + f_\beta + f_\beta^b - 4f_a^b).$$

For the type B_1 .

$$F_{11} = f_d - f_d^d.$$

$$F_{12} = d(f_d^b - f_d'^b).$$

$$F_{22} = d^2(f_\beta - f_\beta^b).$$

For the type B_2 .

$$F_{11} = f_\gamma.$$

Elements of G matrices* obtained with the help of Decius Tables (1948) are as follows.

For the type A_1 .

$$G_{11} = \mu_N + \mu_R.$$

$$G_{12} = \sqrt{2}\mu_N \cos \beta.$$

$$G_{13} = \sqrt{(2/3)}a\mu_N \left\{ \sin \beta - \frac{2 \cos \beta}{\sin \alpha} (1 - \cos \alpha) \right\}$$

$$G_{22} = \mu_0 + \mu_N(1 + \cos \alpha)$$

$$G_{23} = \mu_N/\sqrt{3} \left[\frac{1}{\sin \beta} (a - b \cos \beta) \cos \beta + (b - a \cos \beta)(1 + \cos \alpha) - 2a \sin \alpha \right]$$

$$G_{33} = 1/3[4a^2\{\mu_0 + \mu_N(1 - \cos \alpha)\} + b^2\mu_R + a^2\mu_0 + \mu_N(a^2 + b^2 - 2ab \cos \beta) \\ + b^2\mu_R y + \mu_N\{(b - 2a \cos \beta)by\} + a^2\{\sin^2 \beta(1 - y^2) + y \cos \alpha\} \\ - 4\mu_0 a^2 x - 4\{(a - a \cos \alpha - b \cos \beta)ax + (\sin \alpha \sin \beta(1 - x^2) + x \cos \beta)ab\}\mu_N].$$

For type B_1 .

$$G_{11} = \mu_0 + \mu_N(1 - \cos \alpha).$$

$$G_{12} = -(\mu_N/\sin \beta)(b - a \cos \beta)(1 - \cos \alpha).$$

$$G_{22} = (\mu_R/\sin^2 \beta)b^2(1 - \cos \alpha) + \mu_0 a^2 + (\mu_N/\sin^2 \beta)(b - a \cos \beta)^2(1 - \cos \alpha).$$

For type B_2 .

$$G_{11} = (1/2)\mu_0 \cos^2 \beta + \mu_N \frac{(D-d \cos^2 \beta)}{D^2 \cos^2 \beta} + \mu_R d^2/D^2.$$

In the above expressions

$$a = 1/d, \text{ and } b = 1/D$$

$$x = (\cos \beta - \cos \alpha \cos \beta)/\sin \alpha \sin \beta.$$

$$y = (\cos \alpha - \cos^2 \beta)/\sin^2 \beta.$$

For calculating the g matrix elements the values of bond distances, bond angles and the masses of different atoms are taken from Table I (1958).

TABLE I

Bond distances, interbond angles, masses of different atoms, and moments of inertia of nitril fluoride and nitril chloride

Bond distances			Mass of the atom.
	F-NO ₂	Cl-NO	
N-O (d)	1.22 Å	1.16 Å	$m_0 = 16.00$ (a.w.u.)
N-R (D)	1.50 Å	1.98 Å	$m_N = 14.008$ (a.w.u.)
			$m_{Cl} = 35.457$ (a.w.u.)
			$m_F = 19.000$ (a.w.u.)
Interbond angles			Moments Of Inertia.
<O-N-O (α)	150°	130°	$I_x^F = 40.7369, I_y^F = 44.436, I_z^F = 85.173.$
<R-N-O (β)	105°	115°	$I_x^{Cl} = 110.212, I_y^{Cl} = 35.367, I_z^{Cl} = 145.579$

Note:—The symmetry number for this form is 2.

The moments of inertia are given in units of (a.w.u.Å²).

In the first calculations the force constants derived by Hariharan were used in toto and interaction constants which he has ignored, were proposed by the authors, keeping in view the proper order of the magnitude of such force constants. After a few modifications the observed frequencies were reproduced by calculations with an error within one per cent. The force constants finally proposed by the authors are given in Table II. The six corresponding force constants derived by Hariharan are given for comparison.

The observed and the calculated values of the in-plane fundamental vibrational frequencies of both the molecules are given in Table III. The agreement between the observed and the calculated values is a check on the probable accuracy of the force constants proposed.

III. THERMODYNAMIC PROPERTIES

The heat capacity C_p , heat content $(H_0 - E_0^0)/T$ free energy $-(F_0 - E_0^0)/T$ and entropy S^0 at constant pressure for both the molecules with a rigid rotator and harmonic oscillator approximation for the ideal gaseous state at one atmos-

pheric pressure were calculated for twelve temperatures in 100—1000°K range. The results are given in Tables IV and V.

TABLE II
Potential constants for nitryl fluoride and nitryl chloride

Pot. Constants	Nitryl fluoride		Nitryl chloride	
	Authors	Hariharan	Authors	Hariharan
f_d	12.3	10.86	10.25	9.48
f_D	3.3	3.51	4.19	4.19
f_d^d	2.7	2.04	0.95	0.52
f_D^d	1.5	—	1.0	1.41
f_β	1.10	1.13	0.59	0.62
f_β^d	0.48	—	0.30	—
f_a^a	0.40	—	0.25	—
f_D^β	0.30	—	0.20	—
f_a	0.15	-0.13	0.35	0.36
$f_d'^\beta$	0.12	—	0.10	—
f_D^a	0.10	—	0.06	—
$f_{a\beta}$	0.06	—	0.02	—
$f_{\beta\beta}$	0.05	—	0.03	—

Note :—Bond constants and bond-bond interactions constants are given in md/A, bond-angle interaction constants in md/rad, and angle constants and angle-angle interaction constants are given in mdA/rad².

TABLE III
Observed and calculated values of the fundamental frequencies of nitryl fluoride and nitryl chloride

Type	Nitryl fluoride		Nitryl Chloride	
	Observed	Calculated	Observed	calculated
$A_1(\nu_1)$	1312	1312	1293	1296
$A_1(\nu_2)$	822	828	794	798
$A_1(\nu_3)$	460	459	411	404
$B_1(\nu_4)$	1793	1791	1685	1683
$B_1(\nu_5)$	570	567	367	360

TABLE IV

Heat capacity, heat content, free energy and entropy for nitril fluoride

Temp. (K)	C_p^0	$(H_0-E_0^0)/T$	$-(F_0-E_0^0)/T$	S^0
100	8.11	7.97	43.90	51.87
200	9.86	8.42	49.52	57.95
273	11.42	9.02	52.23	61.25
293	11.82	9.19	52.87	62.07
303	12.02	9.29	53.11	62.40
400	13.64	10.15	55.88	66.03
500	14.90	10.98	58.23	69.22
600	15.88	11.72	60.30	72.02
700	16.62	12.36	62.15	74.51
800	17.19	12.93	63.83	76.76
900	17.64	13.43	65.39	78.82
1000	17.98	13.87	66.83	80.70

TABLE V

Heat capacity, heat content, free energy and entropy for nitril chloride

Temp (K)	C_p^0	$(H_0-E_0^0)/T$	$-(F_0-E_0^0)/T$	S^0
100	8.44	8.04	45.88	53.91
200	10.74	8.80	51.65	60.45
273	12.26	9.53	54.50	64.03
293	12.62	9.73	55.17	65.09
303	12.84	9.85	55.44	65.29
400	14.25	10.73	58.35	69.08
500	15.41	11.56	60.84	72.40
600	16.29	12.27	63.01	75.28
700	16.97	12.91	64.96	77.87
800	17.48	13.44	66.71	80.15
900	17.88	13.91	68.31	82.22
1000	18.20	14.33	69.80	84.13

IV. REFERENCES

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